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COMPLETE SPECIFICATION

Improvements in and relating to Semi-Permeable Membranes useful as Battery Separators

We, W. R. GRACE & Co., a Corporation organized and existing under the laws of the State of Connecticut, United States of America, of 7 Hanover Square, New York 5, New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to semi-permeable membranes useful *inter alia* as battery separators, and to their production.

Storage batteries employ an acid or an alkaline electrolyte, the two most widely used batteries being the lead-acid type and the silver cadmium-alkaline type. Separators are included in the batteries to prevent direct contact between plates of opposite polarity while freely permitting electrolytic conduction. The separator for the acid type of battery is generally comprised of a sheet or web with ribs on at least one side, whilst the separator for the alkaline type of battery is usually a thin sheet or film.

In one aspect the present invention consists in a semi-permeable membrane which is particularly, though not exclusively, useful as a battery separator, having an essentially flat surface and consisting essentially of a micro-porous polyolefin having a standard load melt index (as hereinafter defined) of 0. In another aspect the invention consists in battery separators comprising such semi-permeable membranes. In yet another aspect the invention consists in a process for producing a semi-permeable membrane which comprises blending a composition of from 5 to 65 volume percent

of polyolefin having a standard load melt index (as hereinafter defined) of 0, 5 to 60 volume percent of an inert filler material, and at least 30 volume percent of a plasticizer; forming the composition into a web having at least one essentially flat surface; and extracting from the web a portion of the filler or the plasticizer, or both, to form a porous battery separator.

Although as has been said the new semi-permeable membranes have other uses, it will be convenient to describe the invention in more detail by reference to battery separators comprising them. Such meet minimum resistance requirement and possess acceptable tensile strength and porosity.

The standard load melt index (SLMI) referred to in this specification was measured as specified in ASTM D 1238—57T (Condition E) using a standard load of 2,160 grams. The high load melt index (HLMI) was measured as specified in ASTM D 1238—57T (Condition F) using a load of 21,600 grams.

The battery separator may be provided with rib members and these members can be formed from a number of polymeric compositions, for example the composition of the battery separator, foamed polypropylene, foamed polyethylene, filled foamed polyvinyl chloride or filled foamed polyethylene.

The use of inorganic fillers and extenders for rubbers and some other resins is well known but most attempts to use these fillers to extend polyolefins have met with failure due to the increased crystallinity, which makes the products obtained too brittle to be useful as general purpose resins or as base compositions.

In our Specification No. 1,044,502 and 1,044,028 there are disclosed inexpensive blends of fillers and polyolefins which retain to a surprising extent much of the flexibility, impact resistance, and strength of the base polymers and these compositions are used for the production of battery separators in accordance with this invention.

The polyolefin used in this invention must be substantially insoluble in the solvents used and at the temperatures used to extract the plasticizer or filler from the polyolefin-filler-plasticizer composition. Such insolubility or inertness to the action of solvents is imparted by its crystallinity content or by the judicious choice of solvent used in the extraction procedure. Partially crystalline polyethylene and isotactic polypropylene are ideally suited because they are substantially insoluble in common hydrocarbons and other organic and aqueous solvents at low temperatures.

It is to be understood that conventional stabilizers are incorporated in the compositions of the present invention to prevent thermal and oxidative degradation of the polyolefin component. Representative of the stabilizers are 4,4 - thiobis - (6 - t - butyl - m - cresol) ("Santonox"), and 2,6 - di - t - butyl - 4 - methylphenol ("Ionol").

The polyolefin may be a mixture of a high molecular weight polyolefin with a standard load melt index of 0 and a compatible lower molecular weight polyolefin with a standard load melt index higher than 0. Any amount of the lower molecular weight polyolefin can be used as long as such amount does not raise the standard load melt index of the polyolefin mixture above 0. Ordinarily, the standard load melt index of the lower molecular weight polyolefin will be about 0.1 to about 5. Representative of the polyolefins of both high and low molecular weight which may be used are polyethylene, polypropylene, polybutene, ethylene-propylene copolymers, ethylene-butene copolymers, propylene-butene copolymers and ethylene-propylene-butene copolymers.

The filler should not be soluble in the plasticizer as it provides the primary means by which the plasticizer is absorbed and held in the compositions. The capacity of the filler particles to absorb and hold the plasticizer in the composition is proportional to its surface area which, in turn, depends upon the particle size and degree of porosity. Generally, the size of the filler particles can be from an average of about 0.01 micron to about 10 microns in diameter depending upon the porous character of the filler. The surface area of the filler can be from 30 to 950 square metres per gram, although a surface area of at least 100 square metres per gram is preferred. Ordinarily, amounts of filler used in the composition can be from about 5 to 60 volume percent but the specific amount of filler used will depend

primarily on its surface area and the amount of plasticizer used. The filler can be soluble or insoluble in water. Water-insoluble fillers which may be used are, for example, carbon black, coal dust and graphite; metal oxides and hydroxides such as those of silicon, aluminium, calcium, magnesium, barium, titanium, iron, zinc, and tin; metal carbonates such as those of calcium and magnesium; minerals such as mica, montmorillonite, kaolinite, attapulgite, asbestos, talc, diatomaceous earth and vermiculite; synthetic and natural zeolites; portland cement; precipitated metal silicates such as calcium silicate and aluminium polysilicate; alumina silica gels; wood flour, wood fibres and bark products; glass particles including microbeads, hollow microspheres, flakes and fibres; and salts such as molybdenum disulphide, zinc sulphide and barium sulphate.

Water-soluble fillers which may be used are, for example, inorganic salts such as the chlorides of sodium, potassium, and calcium; acetates such as those of sodium, potassium, calcium, copper and barium; sulphates such as those of sodium, potassium and calcium; phosphates such as those of sodium and potassium; nitrates such as those of sodium and potassium; carbonates such as those of sodium and potassium, and sugar.

When the battery separator contains unextracted filler and is to be used in alkaline batteries then alkali insoluble fillers should be used; similarly, in acid batteries acid insoluble fillers only should be used. Neutral fillers, which do not react with either acid or alkaline electrolytes, can of course be used with either type of battery. Examples of neutral fillers are carbon black, coal dust, graphite and barium sulphate; of alkali insoluble fillers are the oxides, hydroxides and carbonates of calcium, magnesium, barium and iron; and of acid insoluble fillers is silica.

Because of both economic and processing considerations, and its effectiveness in the final product, the preferred filler is dry finely divided silica. It has been found that separators produced from compositions containing this filler have acceptable pore size and void volume and are readily wet by electrolyte.

Generally, battery separators containing hydrophilic fillers such as silica are more readily wet by electrolyte than battery separators containing hydrophobic fillers such as carbon black or battery separators without filler. In such cases any of the commercially available wetting agents, such as sodium alkyl benzene sulphonate, sodium lauryl sulphate, and isooctyl phenyl polyethoxy ethanol, can be used. They can also be used to enhance the wettability of the filler prior to its inclusion in the composition.

The plasticizer improves the processability of the composition, i.e. lowers the melt viscosity or reduces the amount of power input which

is required to compound and to fabricate the composition, and, in addition, since the plasticizer is the component which is easiest to remove from the polymer-filler-plasticizer composition, it is useful in imparting porosity to the battery separators. The plasticizer can be soluble or insoluble in water. Water-insoluble plasticizers are, for example, organic esters such as the sebacates, phthalates, stearates, adipates and citrates; epoxy compounds such as epoxidized vegetable oil; phosphate esters such as tricresyl phosphate; hydrocarbon materials such as petroleum oil, wax, hydrocarbon resin and asphalt and pure compounds such as eicosane; low molecular weight polymers such as polyisobutylene, polybutadiene, polystyrene, atactic polypropylene, ethylene-propylene rubber; ethylene-vinyl acetate copolymer, oxidized polyethylene, coumarone-indene resins and terpene resins; tall oil and linseed oil.

Water-soluble plasticizers are, for example, ethylene glycol, polyethylene glycol, polypropylene glycol, glycerol, and ethers and esters thereof; alkyl phosphates such as triethyl phosphate; polyvinyl alcohol; polyacrylic acid and polyvinyl pyrrolidone.

When a plasticizer is used which is not removed from the composition during the

extraction step but forms part of the battery separator, it imparts flexibility, high elongation and imparts resistance to the battery separator. There are a number of water insoluble, normally solid plasticizers which are sufficiently inert to form a part of the battery separator. Typical examples of these plasticizers are polyisobutylene, polybutadiene, polystyrene, atactic polypropylene, ethylene-propylene rubber and ethylene-vinyl acetate copolymer. Generally, when this type of plasticizer is used it can be included in the battery separator in an amount as high as 40 percent by volume of the composition.

The battery separator, therefore, can consist essentially of a homogeneous mixture of 8 to 100 volume percent of polyolefin having a standard load melt index of 0, 0 to 40 volume percent of a substantially inert solid plasticizer, and 0 to 92 volume percent of inert filler material.

The preferred ranges for the components comprise from 7.5 to 40 volume percent of polyolefin, from 10—40 volume percent filler, and the difference between the total amount of polyolefin and filler and 100 percent being the plasticizer. Examples of particularly preferred compositions are as follows:

| Polyolefin (Vol. %) | Filler (Vol. %) | Plasticizer (Vol. %) |
|------------------------|--------------------|-------------------------|
| 20 | 20 | 60 |
| 20 | 15 | 65 |
| 17 | 18 | 65 |
| 15 | 15 | 70 |
| 10 | 15 | 75 |

The above amounts are based upon the processing requirements of the composition, the physical properties necessary in the final product, and the cost of the composition, and have been found to be acceptable.

A particularly preferred composition consists essentially of polyethylene having a standard load melt index of 0 and at least 50 percent by weight crystallinity, finely-divided silica and petroleum oil.

The components can be mixed by any conventional manner which will produce a substantially uniform mixture. To produce a particularly uniform mixture, the components can be premixed at room temperature in a blender. The polyolefin-filler-plasticizer dry blends are then fluxed in a conventional mixer such as a Banbury mixer or melt homogenized

in a conventional two roll mill.

After being suitable mixed, the composition is moulded or shaped in any conventional manner, such as extrusion, calendering, injection moulding, or compression moulding.

As used in this specification, the term "sheet" is intended to define a unitary article, i.e., a battery separator consisting of a base web and a plurality of rib members. As will be described in detail hereinafter, the web and rib members can be of the same material or of different materials. The term "film" is used to define a battery separator which does not have rib members and which can be very thin. Such a film is particularly suitable for use in alkaline batteries where it generally has a thickness of about 5 mils or less. The term "essentially flat surface" is intended to be

generic to sheets and films and thus to refer to battery separators suitable for use in either acid or alkaline batteries.

The rib members of the battery separator can also be formed by a conventional method. In order to reduce the expense of fabrication, the rib members are preferably of the same composition as the base web or of foamed polypropylene, foamed filled polyvinyl chloride, or foam filled polyethylene. The term "foamed polyethylene" or "foamed polypropylene" defines a polyolefin which has been foamed by conventional techniques, e.g. dry blended with a foaming agent such as azobisformamide plus zinc stearate, pelletized, and extrusion-foamed at a temperature of approximately 375°F. The term "foamed filled polyolefins" or "foamed filled polyvinyl chloride" is intended to define a polymer which has been dry blended with a foaming agent and a filler material such as carbon black or any other fillers mentioned in this specification. This dry blend is then pelletized and foamed. The polyethylene used in the ribs need not be the same type used in the web, but may be of a lower molecular weight and density which may be more readily formed into ribs. When the rib members are made of the same material as the web, the separator may be extruded as a unitary article. Alternatively, the rib members may be formed by passing a web through a pair of embossing rollers to form the ribs on the web as a unitary article. The web can be extracted with solvent before it passed through the embossing rolls to form ribs on the web.

Separate rib members can be bonded to the base web by a number of methods well known in the art, including heat sealing and the use of an adhesive. The rib members may be bonded to the web either before or after the web is extracted with solvent as it has been found that there are no material adverse effects upon the physical properties of the battery separator if the extraction is carried out after bonding.

The extraction procedure and medium employed depends upon the component which is to be extracted. For example, if the plasticizer or the filler only is to be extracted, a single stage extraction is used. If the plasticizer and the filler are both to be extracted, however, a two-stage extraction may be required. A multiple-stage extraction may also be required if two or more dissimilar plasticizers or fillers are used in the same composition.

Numerous extracting solvents are suitable, depending upon the particular ingredient to be extracted, providing that the solvent or extraction conditions are chosen so that the polyolefin is essentially insoluble. For example, when petroleum oil is to be extracted from the moulded composition, the following solvents are suitable: chlorinated hydrocarbons, such as trichloroethylene, tetrachloroethylene, carbon tetrachloride, methylene chloride, and

tetrachloroethane; hydrocarbon solvents such as hexane, benzene, petroleum ether, toluene, cyclohexane or gasoline. If polyethylene glycol is to be extracted, the extraction medium can be water, ethanol, methanol or acetone. If finely-ground silica is to be extracted, the following solvents are suitable: aqueous or alcoholic sodium hydroxide or potassium hydroxide or hydrofluoric acid solution. Generally, acids such as hydrochloric acid can be used to extract metal oxides and metal carbonates. The extraction temperature can be from room temperature up to the melting point of the polyolefin providing the polyolefin does not dissolve.

The time of the extraction will vary depending upon the temperature used and the nature of the plasticizer or filler being extracted. For example, when a higher temperature is used, the extraction time for an oil of low viscosity can be only a few minutes, whereas if the extraction is performed at room temperature the time required for a polymeric plasticizer can be in the order of several hours.

The final composition of the separator will depend upon the original composition and the component or components extracted. When the plasticizer and the inert filler are removed from the moulded composition, the microporous battery separator will consist essentially of polyolefin having a standard load melt index of 2. When the moulded composition consists of 5 to 65 volume percent of polyolefin, 5 to 60 volume percent filler and the remainder is plasticizer, and only the plasticizer is extracted from the composition, the battery separator will consist of 8 to 93 volume percent polyolefin and 7 to 92 volume percent filler. When the moulded composition consists of 7.5 to 40 volume percent of polyolefin, from 10 to 40 volume percent of filler and the remainder is plasticizer, and only the plasticizer is removed from the composition, the battery separator will consist of 15.8 to 80 volume percent polyolefin and 84.2 to 20 volume percent filler.

The particularly preferred battery separators consist of 40 to 60 volume percent of polyolefin having a standard load melt index of 0, and 40 to 60 volume percent inert filler.

The microporous battery separators of this invention have a pore size which is generally less than 1 micron in diameter, preferably with greater than 50% of the pores being 0.5 micron or less in diameter. In most cases, at least 90% of the pores have a diameter smaller than 0.5 micron.

Unless otherwise stated, the pore size and the pore volume quoted in this specification were measured using the mercury intrusion method described in Ritter, H. L., and Drake, L. C., *Ind. Eng. Chem. Anal. Ed.*, 17, 787 (1945).

According to this method, mercury is forced into different sized pores by varying the pressure exerted on the mercury, i.e., low

pressures fill large sized pores and higher pressures fill small sized pores. The total pore volume is then determined and the pore volume distribution calculated from a measure of mercury in the various sized pores and the pressures exerted. Such a determination was accomplished using a standard commercial mercury porosimeter (Aminco-Winslow Porosimeter). The pore diameter entered by the mercury under pressure is stated in the equation:

$$D = \frac{175}{P}$$

where D is the diameter of the pore in microns and P is absolute pressure in pounds per square inch. According to the equation, 350 psi is required to force the mercury into pores having a diameter of 0.5 micron. Since pressures higher than 350 psi may collapse some pores and compress the samples in the present invention, pores having a diameter smaller than 0.5 micron may not be accurately measured by this method.

Mercury intrusion data for commercial battery separators of various materials were compared to data obtained for battery separators prepared according to the present invention. The results are shown in Table I.

TABLE I

| Pore Diameter Microns | MERCURY INTRUSION OF BATTERY SEPARATORS | | | | | |
|----------------------------|---|------------------------|-----------------------------|------------------------|-----------|-----------|
| | Volume Percent of Pores | | | | | |
| | Microporous Polyvinyl Chloride | Rubber Silica Hydrogel | Sintered Polyvinyl Chloride | Polyethylene Cellulose | Example 1 | Example 5 |
| .035—.05 | 0 | 3.6 | 0 | 0 | 25.0 | 11.9 |
| .05—.1 | 1.05 | 5.1 | 1.2 | 0.5 | 33.9 | 27.0 |
| .1—.3 | 0 | 10.3 | 1.2 | 0.5 | 26.8 | 53.8 |
| .3—.5 | 1.05 | 8.7 | 0 | 0.5 | 7.1 | 2.3 |
| .5—.7 | 0 | 7.4 | 0 | 0.5 | 1.8 | 1.1 |
| .7—1.0 | 2.1 | 10.2 | 0 | 0.5 | 1.8 | 1.1 |
| 1.0—2.0 | 16.0 | 23.2 | 0 | 1.4 | 1.8 | 1.1 |
| 2.0—3.0 | 71.3 | 15.4 | 0 | 1.9 | 1.8 | 0.9 |
| 3.0—4.0 | 7.4 | 6.0 | 0 | 1.4 | 0 | 0 |
| 4.0—5.0 | 1.1 | 2.9 | 1.2 | 2.4 | 0 | 0.9 |
| 5.0—10 | 0 | 3.5 | 3.3 | 10.0 | 0 | 0 |
| 10—50 | 0 | 2.3 | 82.0 | 77.5 | 0 | 0 |
| 50—100 | 0 | 1.4 | 11.1 | 2.9 | 0 | 0 |
| Mean Pore Diameter Microns | 2.58 | 1.18 | 36.7 | 16.6 | 0.084 | 0.14 |

In Example 1 of Table I the composition consisted of 20 volume percent of polyethylene, 20 volume percent of silica and 60 volume percent of polyethylene glycol. The polyethylene glycol was extracted with water. In Example 5 of Table I the composition consisted of 15 volume percent of polyethylene,

15 volume percent of silica and 70 volume percent of petroleum oil. The petroleum oil was extracted with trichloroethylene.

To show the presence of exceedingly small pores in the structure of the battery separators of the present invention, i.e. pores having a diameter in the range of 0.002 to 0.06 microns

in diameter, the nitrogen absorption method described by S. Brunauer, P. Emmett and E. Teller in J. Am. Chem. Soc., 60, 309 (1938) was used.

5 The nitrogen absorption test was used to

determine the surface area and pore diameter of battery separators of various materials including battery separators prepared according to the instant invention. The results are shown in Table II.

10

TABLE II

Nitrogen Absorption Test

| Battery Separator Material | Surface Area (Sq. metres/gram) | Mean Pore Diameter (Microns) |
|---|-----------------------------------|------------------------------------|
| Rubber-silica hydrogel | 92 | .027 |
| Sintered Polyvinyl Chloride | 9 | Poros too large to measure |
| Example 5 (15% by vol. polyethylene, 15% by vol. silica and 70% by vol. petroleum oil before extraction) | 135 | .011 |

As illustrated in Table II, the battery separator prepared according to this invention has a larger surface area and a smaller mean pore diameter than battery separators prepared from two conventional materials. The smaller mean pore diameter shows clearly the presence of exceedingly small pores in the structure of the battery separators prepared according to this invention.

The size of the pores satisfies the requirements of battery separators in general that the size of the pores be small enough to prevent the passage of solid materials such as lead of lead sulphate crystals but sufficiently large to permit the electrolyte to pass through. In addition, the pores are small enough to hinder the passage of antimony ions which frequently are introduced into the electrolyte by the positive plate and which migrate to the negative plate and thereby shorten the life of the battery.

The minute pore size of the separators of this invention is in distinct contrast (see Table II) so that of presently available commercial microporous separators. In addition, the void volume of the separators can be greater than that of most commercial separators (see Table II).

The void volume can vary to a considerable extent depending upon the particular ingredients and thickness of the separator. For example, if the separator is very thin, a void volume as low as 30% is acceptable but it is

normally desirable, however, that the void volume of the separator be at least 50% and preferably 70 to 80%. The combination of extremely small pore size and high void volume in a battery separator which surpasses minimum resistance requirements and which possesses excellent physical and chemical properties is very unexpected. These unexpectedly superior properties are believed to be the result of the use of the very high molecular weight polyolefin which gives strength to the final product. Evidence of this is apparent from a comparison of Examples 4 and 9, good results being obtained with polyethylene having a standard load melt index of 0, as compared to those obtained with a low molecular weight polyethylene having a standard load melt index of 0.7.

Table III is a comparison of the average pore diameter and void volume of a separator of this invention prepared as described in Example 2 and commercial separators. In Example 2 the composition consisted of 10% by volume of polyethylene having a standard load melt index of 0; 15% by volume of silica and 75% by volume of petroleum oil. The petroleum oil was extracted from the moulded composition with petroleum ether and the void volume shown in Table III is based on the extracted amount of petroleum oil. The average pore diameter of the separator of Example 2 was measured by mercury intrusion on an Aminco-Winslow Porosimeter.

TABLE III

| Separator | Average Pore Diameter Microns | Void Volume* % |
|--------------------------------|-------------------------------------|-------------------|
| Sintered Polyvinyl Chloride | 36.7 | 48 |
| Microporous Polyvinyl Chloride | 2.58 | 87 |
| Rubber/Silica Hydrogel | 1.18 | 66 |
| Polyethylene Cellulose | 33.0 ^a | 70 |
| Standard Cellulose | 40.0 | 67 |
| Example 2 | 0.11 | 75 |

* Values are taken from a paper by Robinson and Walker, Third International Battery Symposium, Bournemouth, England, October, 1963, except for the value for Example 2.

^a Value was taken from reference cited above (*).

5 The thickness of the battery separators will vary depending upon the type of battery in which they are used. In general, the thickness of the base web can range from 1 to 50 mils. For lead-acid batteries, the preferred thicknesses range is usually 10 to 40 mils. The rib members for lead-acid battery separators should be from 5 to 200 mils in height from the base web, the preferred range being 10 to 100 mils. For alkaline type batteries, the preferred thickness is generally about 1 to 10 mils.

10 In order to be commercially acceptable, battery separators must meet minimum resistance requirements. Generally, the acceptable range is from 1 to 100 milliohms-square

inch, with the preferred range being from 10 to 60 milliohms-square inch. They must also possess certain physical properties, such as tensile strength, puncture strength, break angle strength, and pore volume.

20 Battery separators should possess chemical properties such as resistance to oxidation, and resistance to loss of weight in acid in order to be suitable for commercial usage. To demonstrate the superior qualities of the separators of this invention, samples made from a polyethylene-filler-plasticizer blend were subjected to these tests and compared with other commercial separators. The results are summarized in Table IV.

TABLE IV

| Separator | Oxidation Test ¹ (hours) | Acid Weight Loss ² | Fast Acid Weight Loss ³ |
|--------------------------------|-------------------------------------|-------------------------------|------------------------------------|
| ⁴ | 227 + | 1.6% | 0.5% |
| ⁵ | 227 + | 0.6% | — |
| Sintèred Polyvinyl Chloride | 227 + | 1.5% | 2.7% |
| Microporous Polyvinyl Chloride | 227 + | 61.3% | 28.6% |
| Rubber/Silica Hydrogel | 208 | 8.6% | Destroyed |
| Polyethylene Cellulose | 114 | 31.0% | 44.8% |

¹ Oxidation test was made at ambient temperatures by placing the separator between electrodes, immersing the resulting assembly in a sulphuric acid solution having a specific gravity of 1.400, passing a current of 9 amperes through the circuit which provided a current density of 3 amperes per square inch, and maintaining the current of 9 amperes until short circuiting occurs.

² 168 hours in 1.3000 sp. gr. H₂SO₄ at 165° F.

³ 3 hours at 140° F. in 3% potassium dichromate in 1.200 sq. gr. H₂SO₄.

⁴ This is Example 18. 17 vol. % polyethylene (SLMI = 0, HLMI = 0), 18 vol. % finely ground silica, 44 vol. % glycerin and 21 vol. % petroleum oil was processed into a sheet 0.028 inch thick and the glycerin and paraffin oil were extracted with water and petroleum ether.

⁵ Same as ⁴, but thickness was 0.020 inch.

As noted in Table IV, there is significantly less loss of material in acid with the separators made from the polyethylene-filler-plasticizer blends of the invention than with the commercial separators.

This invention is further illustrated by the following Examples. Unless otherwise stated, tests in the following Examples were made as follows: the tensile strength of the samples was measured by a standard commercial tensile tester which continually records stress as it pulls the sample at a constant rate of strain. Unless otherwise specified, the tensile strength of the sample was measured in the extrusion direction of the sample.

The resistance to puncture of the samples was measured as follows: a $\frac{1}{4}$ inch diameter probe (connected via a lever arm to a container) with a rounded end is placed on the sample. Water is added to the container above

the probe on the lever arm until the sample is punctured. The weight of water added is recorded.

The samples were also subjected to a break angle test. The purpose of this test is to determine the flexibility of the samples by measuring the angle at which the sheet breaks when bent by hand.

The samples were also tested to determine their pore volume and average pore diameter. Unless otherwise stated these were determined according to the mercury intrusion method on an Aminco-Winslow Porosimeter.

The crystallinity of the polyolefins was determined by an X-ray diffraction method described by J. L. Matthews, H. S. Pieser and R. B. Richards in Acta Crystallographica 2, 85—90 (1949). According to this method, the crystallinity of the polyolefins was determined to be as follows:

| | |
|---------------------------------|--|
| polyethylene ("Grex FF-60-018") | particle form 72 to 75% by weight |
| polyethylene ("Hifax 1901") | particle form 83.3% by weight pressed sheet 58.4% by weight |
| polypropylene | particle form 45.6% by weight pressed sheet 45.7% by weight annealed sheet 51.5% by weight quenched sheet 35.8% by weight |

EXAMPLE 1.

The polyethylene ("Grex FF-60-018") used in this Example had a standard load melt index of 0, a high load melt index of 1.8, a density of 0.95, and a reduced specific viscosity of 4.0. The viscosity was measured with a solution of 0.02 gram of the polyethylene in 100 grams of decalin at 130°C. The filler was a finely divided silica ("HiSil 233"; "HiSil" is a Registered Trade Mark) having an average particle diameter of about .02 micron and a surface area of 165 square meters per gram.

Using the system described, a composition consisting of 20 volume percent of the polyethylene having a standard load melt index of 0, 20 volume percent of silica, 60 volume percent polyethylene glycol of 4,000 molecular weight ("Polyglycol E, 4000"), and the antioxidant, phenothiazine, in an amount of 0.05 percent by weight of the composition (0.36 percent by weight of the polyethylene), was mixed in a two roll mill for a period of about 10 minutes and removed in sheet form. After grinding in a Wiley mill, the composition was fed to the hopper of a one-inch extruder which was operating at a speed of 70 r.p.m. and at a pressure of 400 psi. Attached to the extruder was an eight inch sheeting die. The temperature profile which was progressively spaced along the length of the extruder from the feed end to the die end was 200°F., 350°F. and 350°F. The extruder was adjusted so as to operate at a speed of approximately 1½ feet per minute. The extruded composition was then immersed in water for 20 hours at 130°F. to extract the polyethylene glycol plasticizer. The thickness of the final product was found to be 49 mils.

The polyethylene silica sample was then analyzed by standard techniques to determine its resistance. The electrical resistance was found to be 70 milliohms-square inch. When subjected to the puncture test, it was found that the sample was able to withstand a force of 673 grams. The tensile strength of the sample was 210 lbs. per square inch. The break angle of the sample was 85 degrees. The pore volume was 0.30 cc./g. The mean pore diameter was 0.084 micron.

EXAMPLE 2.

The procedure of Example 1 was followed using the polyethylene and the silica of Example 1. A composition consisting of 10% by volume of the polyethylene, 15% by volume of the silica, 75% by volume of petroleum oil ("Shellflex 411", 547 SSU at 110°F.) and the antioxidant, 2,6-di-t-butyl-4-methylphenol ("Ionol") in an amount of 0.1 percent by weight of the composition (1.15 percent by weight of the polyethylene), was blended on a two roll mill for about 5 minutes and removed as sheet. After grinding on a Wiley mill, the composition was fed into the hopper of a standard one-inch extruder to which was attached an eight inch sheeting die. The pressure within the extruder was 500 psi. The temperature profile along the length of the extruder from the feed end to the die end progressively decreased from 400° to 300°F. with the die at 350°F. The extrusion rate was again approximately 1½ feet per minute. The extruded composition was then immersed in petroleum ether for 60 minutes at room temperature to extract the petroleum oil. The thickness of the final product was 26 mils.

This sample was then tested to determine its properties. Resistance of this sample was found to be 22 milliohms-square inch. The puncture test indicated that this sample could withstand a force of 366 grams. The tensile strength was 220 lbs. per square inch. The break angle was found to be greater than 110°. The pore volume was determined to be 0.71 cc./g. The mean pore diameter was 0.11 micron.

EXAMPLE 3.

The procedure of Example 1 was generally followed using the polyethylene, silica and petroleum oil used in Example 2. A composition consisting of 20 volume percent of the polyethylene, 15% by volume of the silica, and 65% by volume of petroleum oil was mixed in a two-roll mill for about 5 minutes and removed as sheet. The product was immersed in trichloroethylene for 60 minutes at room temperature to remove the petroleum oil. The thickness of the final product was 23 mils.

The resistance of this sample was found to be 66 milliohms-square inch. This sample was

able to withstand a force of 1313 grams. The tensile strength was 580 lbs. per square inch. The break angle was greater than 110°. The pore volume was 0.76 cc./g. The mean pore diameter was 0.12 micron.

EXAMPLE 4.

The polyethylene, silica and petroleum oil used in this Example were the same as used in Example 2.

A composition consisting of 17% by volume of the polyethylene, 18% by volume of the silica, 21% by volume of petroleum oil, 44% by volume glycerol and 2,6-di-6-butyl-4-methylphenol ("Ionol") in an amount of 0.1 percent by weight of the composition was pelletized by extrusion. This composition was then fed to an extruder to which was attached an eight inch sheeting die. The extruder was operated at a speed of 60 rpm. and at a pressure of 550 psi. The temperature profile from the feed end to the die end progressively increased from 300°F. to 350°F. The extruded product was immersed in water for 6 hours at room temperature to extract the glycerol. The resulting product was then immersed for 1 hour in petroleum ether to extract the petroleum oil. The thickness of the final product was approximately 37 mils.

The resistance of this product was 64 milliohms-square inch. This product was able to withstand a force of 1573 grams. The tensile strength of the product was 535 lbs. per square inch. The percent elongation at failure was 35%. The break angle was greater than 150°. The pore volume was found to be 0.41 cc./g. The mean pore diameter was 0.10 micron.

EXAMPLE 5.

The polyethylene, silica and petroleum oil used in this Example were the same as used in Example 2.

A composition consisting of 15% by volume of the polyethylene, 15% by volume of the silica, 70% by volume of the petroleum oil, and 2,6-di-t-butyl-4-methylphenol ("Ionol") in an amount of 0.1 percent by weight of the composition (0.77 percent by weight of polyethylene), was mixed on a two roll mill for about 5 minutes, and removed as sheet. After grinding, the composition was fed to an extruder which was operating at approximately 60 rpm. and at a pressure of 400 psi. An eight inch sheeting die was attached to the extruder. The temperature profile within the extruder progressively decreased from a temperature of 375°F. at the feed end to 300°F. with the die at 325°F. The extrusion rate was again approximately 1½ feet per minute. The extruded product was then immersed in trichloroethylene at 180°F. for 90 minutes to extract the oil. The thickness of the final product was found to be 32 mils.

The resistance of this product was found to be 36 milliohms-square inch. This product

was able to withstand a force of 1013 grams. The tensile strength of the product was 375 lbs. per square inch. The break angle was greater than 110°. The pore volume was found to be 0.88 cc./g. The mean pore diameter was 0.14 micron.

EXAMPLE 6.

The silica and petroleum oil used in this Example were the same as used in Example 2. The polyethylene ("Hifax 1901") had a standard load melt index of 0, a high load melt index of 0, a density of 0.94 grams/cc. and a reduced specific viscosity of 15.

A composition consisting of 10 volume percent of the polyethylene, 15 volume percent of the silica, 75% by volume petroleum oil, and the antioxidant, 2,6-di-t-butyl-4-methylphenol ("Ionol") in an amount of 0.1 percent by weight of the composition was mixed in a Brabender Plastograph for 15 minutes. This composition was then compression moulded. The product was then immersed in petroleum ether for 60 minutes at room temperature to remove the petroleum oil. The thickness of the final product was 33 mils.

The resistance of this sample was 32 milliohms-square inch. The sample could withstand a force of 1973 grams. The tensile strength was 430 lbs. per square inch. Break angle was greater than 110°.

EXAMPLE 7.

The polyethylene, silica and petroleum oil used in this Example were the same as used in Example 2.

Using the system described, a composition consisting of 14.5 volume percent of the polyethylene, 14.5% by volume of the silica, 2.5% by volume of carbon black ("Elftex 8") having an average particle size of 0.03 micron in diameter, and 68.5% by volume of petroleum oil was mixed in a two roll mill for about 5 minutes and removed as sheet. After grinding the sheet, the composition was fed into the hopper of an extruder which was operating under approximately the same conditions as in Examples 2 and 3. The extruded product was then immersed in trichloroethylene for 10 minutes at 180°F. to extract the petroleum oil. The thickness of the final product was 32 mils.

The resistance of this product was determined to be 48 milliohms-square inch. The product was able to withstand a force of 1143 grams. The tensile strength of the product was 415 lbs. per square inch. The break angle was greater than 110°.

EXAMPLE 8.

The polyethylene used in this Example was the same as used in Example 6.

A composition consisting of 20 volume percent polyethylene, 12% by volume of carbon black ("Elftex 8") having an average particle size of 0.03 micron in diameter, and 68% by

volume paraffin oil ("Primol", 335 SSU. at 110°F.) was mixed in a Brabender Plastograph for 15 minutes. The composition was compression moulded and a thin film blown on a "Cryovac" hat tester. ("Cryovac" is a Registered Trade Mark). Briefly stated, this operation comprised securing the outer periphery of the 20 mil thick film in the apparatus, heating the film and then projecting compressed air against one wall of the heated film to form a bubble to draw its wall to the desired thickness.

The sample was immersed in petroleum ether at room temperature to extract the paraffin oil. The thickness of the final product was about 1 mil.

The product had an electrical resistance of 4 milliohms-square inch after treatment with wetting agent.

EXAMPLE 9.

To illustrate the importance of the high molecular weight of the polyethylene having a standard load melt index of 0, this run was conducted using a commercial pelletized polyethylene ("Grex 60007 E") having a standard load melt index of 0.7. Except for the polyethylene component, this composition was the same as that of Example 4. 17 volume percent of the polyethylene of standard load melt index of 0.7, 18% by volume silica, 21% by volume petroleum oil and 44% by volume glycerol was mixed in a Brabender Plastograph for 15 minutes. This composition was then compression moulded and immersed first in water and then in petroleum ether as described in Example 4 to extract the glycerol and petroleum oil. The thickness of the product was 31 mils.

The resistance of the sample was 60 milliohms-square inch. The tensile strength was 287 lbs. per square inch. The percent elongation at failure was 1%.

EXAMPLE 10.

The procedure of Example 1 was generally followed but the polyethylene and petroleum oil used in this Example were the same as disclosed in Example 2. The composition consisted of 15 volumes percent of polyethylene, 69 volume percent of petroleum oil, 15 volume percent of diatomaceous earth ("Celite Filter Cel") having an average particle diameter of 4 microns and a surface area of 25 square metres per gram, 1 volume percent of carbon black ("Sterling MT") having an average particle diameter of 0.47 micron and a surface area of 6 square metres per gram and the antioxidant, 4,4-thiobis-(6-*t*-butyl-*m*-cresol) ("Santonox") in an amount of 0.1 percent by weight of the polyethylene.

The composition was blended, ground and extruded substantially as described in Example 1. The extruded composition was then immersed in petroleum ether for 30 minutes at room temperature to extract the petroleum

oil. The thickness of the final product was 18 mils.

The product was then tested to determine its properties. It was able to withstand a force of 1260 grams of water. The product had a tensile strength of 500 psi in the extrusion direction and 910 psi in the cross-extrusion direction. It had a break angle greater than 110°. The electrical resistance of the product was greater than 100 milliohms-square inch. However, after the product was soaked in a 1% solution of a standard commercial wetting agent for 60 minutes, its resistance was 27 milliohms-square inch.

EXAMPLE 11.

The procedure of Example 1 was generally followed but the polyethylene, silica and petroleum oil used in this Example were the same as those used in Example 2. The composition consisted of 15 volume percent of polyethylene, 69 volume percent of petroleum oil, 15 volume percent of silica, 1 volume percent of carbon black ("Sterling MT") having an average particle diameter of 0.47 micron and a surface area of 6 square metres per gram and the antioxidant 4,4-thio-(6-*t*-butyl-*m*-cresol) ("Santonox"), in an amount of 0.1 percent by weight of the polyethylene.

The composition was blended, ground and extruded substantially as described in Example 1. The extruded composition was then immersed in petroleum ether for 30 minutes at room temperature to extract the petroleum oil. The thickness of the final product was 29 mils.

The product was then tested to determine its properties. It was able to withstand a force of 1100 grams of water. The product had a tensile strength of 430 psi in the extrusion direction and 510 psi in the cross-extrusion direction. It had a break angle greater than 110°. The electrical resistance of the product was 44 milliohms-square inch. However, after the product was soaked in a 1% solution of a standard commercial (e.g. sodium dodecyl benzene sulphonate) wetting agent for 60 minutes, its resistance was 28 milliohms-square inch.

EXAMPLE 12.

The polyethylene and petroleum oil used in this Example were the same as those disclosed in Example 2. The composition consisted of 20 volume percent of polyethylene, 60 volume percent of petroleum oil, 20 volume percent of precipitated calcium carbonate ("Purecal U") having an average diameter of .040 micron and 2,6-di-*t*-butyl-methylphenol ("Ionol") in an amount of 1.0 percent by weight of the polyethylene.

The composition was blended in a Banbury mixer and then placed in a platen press and pressed at about 350°F. at a pressure of 40,000 lbs. for about 3 minutes. The resulting film, which was 20 mils thick, was then blown

into a thin film by means of a "Cryovac" hat tester as described in Example 8.

The resulting film was less than 5 mils thick. This thin film was then immersed in petroleum ether for 30 minutes at room temperature to extract the petroleum oil. The resulting product had a resistance of 8 milliohms-square inch.

EXAMPLE 13.

The procedure and composition used in this Example were the same as those described in Example 12 except that 15 volume percent of polyethylene, 15 volume percent of precipitated calcium carbonate and 70 volume percent of petroleum oil were used. The resulting product, a film less than 5 mils thick, had a resistance of 35 milliohms-square inch.

EXAMPLE 14.

The polyethylene and petroleum oil used in this Example were the same as those disclosed in Example 2. The composition consisted of 30 volume percent of polyethylene, 40 volume percent of petroleum oil, 30 volume percent of a very finely-divided kaolin clay ("Clemson Clay") ordinarily used as filler in paper, and 2,6-di-t-butyl-4-methylphenol ("Ionol") in an amount of 0.1 percent by weight of the polyethylene.

The composition was blended in a Banbury mixer and then blown into a thin film. In this blowing operation, the blend was extruded into a tube, and while the tube was still hot, compressed air was injected into it to form a bubble to draw its wall to the desired thickness. The bubble was then collapsed and slit.

The blown thin film was about one mil thick. It was immersed in petroleum ether for 30 minutes at room temperature to extract the petroleum oil. The resulting film had an electrical resistance of over 100 milliohms-square inch. However, after the film was soaked in a 1% solution of a standard commercial wetting agent solution (e.g. sodium dodecyl benzene sulphonate) for 60 minutes, its resistance was 15 milliohms-square inch.

EXAMPLE 15.

The petroleum oil and silica used in this Example were the same as those disclosed in Example 2. A composition consisting of 15 volume percent polypropylene having a standard load melt index of 0, 15 volume percent of silica, 70 volume percent of petroleum oil and an antioxidant were thoroughly mixed in a Brabender Plastograph. The antioxidant was comprised of 2,6-di-t-butyl-4-methylphenol ("Ionol") in an amount of 0.5 percent by weight of the polypropylene, dialkylthiodipropionate in an amount of 0.5 percent by weight of the polypropylene and calcium stearate in an amount of 0.2 percent by weight of the polypropylene.

The mixture was placed in a platen press

and pressed at about 350°F., at a pressure of 40,000 lbs. for about 3 minutes. The resulting film was immersed in petroleum ether at room temperature for 60 minutes to extract the petroleum oil. The thickness of the final product was 25 mils.

The electrical resistance of the product was determined to be 47 milliohms-square inch.

EXAMPLE 16.

The petroleum oil and silica used in this Example and the procedure were the same as those disclosed in Example 15.

The composition consisted of 15 volume percent of a 99 mole percent ethylene-1 mole percent butene copolymer ("Grex FF-60-018") having a standard load melt index of 0, a high load melt index of 1.7 and a crystallinity of over 50 percent by weight, 15 volume percent of silica, 70 volume percent of petroleum oil and 2,6-di-t-butyl-4-methylphenol ("Ionol") in an amount of 1.0 percent by weight of the copolymer. The thickness of the final product was 22 mils.

The resistance of this product was determined according to the standard technique except that it was pre-soaked under a vacuum of 27 inches of mercury. The electrical resistance was 50 milliohms-square inch. The product had a tensile strength of 440 psi. It was able to withstand a force of 486 grams in the puncture resistance test.

EXAMPLE 17.

In this experiment the battery separator prepared as described in Example 11 was provided on one side with a plurality of ribs of foamed polyethylene.

A composition consisting of 100 parts of a polyethylene having a density of 0.92, 1 part of a blowing agent, azo-bis-formamide ("Kem-pore 150"), 0.5 part zinc stearate and 1.6 parts of carbon black was mixed thoroughly. The mixture was extruded at a temperature of about 155°C., i.e. a temperature below the decomposition temperature of the blowing agent which was 175°C. The extruded mixture was cooled and cut to form pellets.

The pellets were then passed through an extruder maintained at a temperature above the decomposition temperature of the blowing agent, i.e. 180°C., to form a plurality of thin ribs of foamed polyethylene. The ribs were deposited on one side of the battery separator which had been preheated to a temperature of about 80°C. The composite was allowed to cool to room temperature. Good adhesion of the ribs to the separator was obtained.

EXAMPLE 18.

The polyethylene, petroleum oil and silica used in this Example were the same as disclosed in Example 6.

A composition comprised of 17 volume percent of polyethylene, 18 volume percent silica,

21 volume percent petroleum oil, 44 volume percent glycerol, and 2,6-di-t-butyl-4-methyl-
cent by weight of the composition (0.95 percent
cent by weight of the composition (0.95 percent
5 by weight of the polyethylene) was mixed in
a Banbury for about five minutes. A portion
of the resulting composition was compression
moulded to form a sheet 28 mils thick. A
second portion of the resulting composition was
10 compression moulded to form a sheet 20 mils
thick.

Each sheet was immersed in petroleum ether
for one hour at room temperature to remove
the petroleum oil. The sheet was then im-
mersed in water at room temperature for about
15 16 hours to extract the glycerol.

The electrical resistance of the 28 mil thick
sheet was determined to be 49 milliohms-
square inch. The electrical resistance of the
20 20 mil thick sheet was determined to be 20
milliohms-square inch.

EXAMPLE 19.

The composition used in this Example was
the same as described in Example 18 and was
25 mixed and compression moulded to form a
sheet as disclosed in Example 18.

The sheet was immersed in petroleum ether
for one hour at room temperature to remove
the petroleum oil. The sheet was then im-
mersed in water at room temperature for about
30 16 hours to remove the glycerol. At the end
of this time, it was removed from the water
and immersed in about 25% potassium
hydroxide solution for about 16 hours to
35 extract the silica. The sheet was then washed
off with water.

The sheet was 27 mils thick and had an
electrical resistance of 7 milliohms-square inch.
It was able to withstand a force of 510 grams
of water. The tensile strength of the sheet
40 was 160 psi.

EXAMPLE 20.

The lead storage battery used in this Ex-
ample was a conventional 12 volt 60 ampere
45 hours battery containing positive plates of
lead dioxide paste supported on grids of lead
antimony alloy and negative plates of lead
paste on grids of lead antimony alloy. The
plates separated by the separators being tested
50 were immersed in an electrolyte of sulphuric
acid (1.260 gravity acid).

At the end of a period of discharge, the
battery may be converted to its initial condi-
tion, i.e. it can be charged, by providing it

with a current in the opposite direction from
an outside source. As the battery discharges,
a portion of the sulphuric acid is converted to
water and lead sulphate deposits on both
plates. When the battery is charged, the lead
sulphate on the negative plate is converted to
60 lead and the lead sulphate on the positive
plate is converted to lead dioxide. Theoretic-
ally, this procedure converts the battery to its
initial condition.

During the charge discharge cycles of the
battery, the antimony dissolves from the posi-
tive grid, migrates through the sulphuric acid
electrolyte and the battery separator, and
deposits on the negative plate. This deposit
causes local self discharge of the negative plate
which results in a loss in capacity of the
battery. At least part of the lead sulphate pro-
duced during this self discharge is formed
irreversibly. Thus the battery loses some of
its capacity permanently. 75

The battery separator used in this Example
was prepared substantially as described in
Example 17. This separator was placed in the
lead storage battery and its effectiveness in
preventing antimony ion transfer during
80 "charge" "discharge" cycles of the lead storage
battery was tested. The same test was also
conducted with a number of commercial
battery separators.

The test used in this Example to determine
the effectiveness of the separator of the inven-
tion in preventing the deposition of antimony
on the negative plates is described in Robinson,
R. G., and Walker, R. L., "Separators and
Their Effect on Lead-Acid Battery Perform-
ance", in Collins, D. H., Ed. *Batteries*, Mac-
Millan Co., N.Y., 1963, p. 28. One complete
cycle of this test is comprised of the following:

- (a) 4½ days' continuous charge at the normal
rate of 3 amperes at 70°F. 95
- (b) 7 days' stand on open circuit at 100°F.
- (c) A discharge at the 10 hour rate to 1.8
volts per cell at 70°F.
- (d) A full recharge.
- (e) A discharge at the 10 hour rate to 1.8
100 volts per cell at 70°F.

From the discharges under (c) and (e) the
percentage loss in capacity during the 7 days'
open circuit stand was calculated.

The percentage capacity loss at the end of
the sixth cycle was determined and the results
were as follows: 105

| Battery Separator | Percent Capacity Loss at End of Sixth Cycle |
|--|--|
| Battery Separator prepared substantially as described in Example 17 | 17 |
| Microporous Rubber | 28 |
| Microporous Polyvinyl Chloride ("Porvic 1") | 21 |
| Sintered Polyvinyl Chloride ("Porvic 2B") | 75 |
| Rubber and Diatomaceous Silica backed with Spun Glass Fibre Mat ("Permalife") | 43 |

The above results show a significantly lower loss in capacity for the battery using the separator prepared according to this invention.

- 5 It is thus seen that the invention provides a novel and relatively inexpensive battery separator of superior quality, and which is suitable for use in batteries employing an acid electrolyte such as, for example, the lead acid type, and also in batteries employing an alkaline electrolyte such as the silver-zinc or nickel-cadmium types.

- 10 It is clear that the process of this invention may be operated in a continuous manner when in actual production.

- 15 Although the invention is described in connection with battery separators, it can easily be adapted for other uses requiring a product of similar physical characteristics such as selective filtration membranes and breathable coatings for textile fabrics such as rainwear.

WHAT WE CLAIM IS:—

1. A semi-permeable membrane having an essentially flat surface and consisting essentially of a microporous polyolefin having a standard load melt index (as hereinbefore defined) of 0.

- 25 2. A semi-permeable membrane according to claim 1, wherein the polyolefin is polyethylene, polypropylene, polybutene, an ethylene-propylene copolymer, an ethylene-butene copolymer, a propylene-butene copolymer, or an ethylene-propylene-butene copolymer.

- 30 3. A semi-permeable membrane according to claim 1 or 2, wherein the polyolefin consists essentially of a blend of a high molecular weight polyolefin having a standard load melt index of 0 and a low molecular weight polyolefin having a standard load melt index of 0.1 to 5.

- 40 4. A semi-permeable membrane according to claim 3, wherein each of the blend components is polyethylene.

- 45 5. A semi-permeable membrane according to any of claims 1 to 4, consisting of a homogeneous mixture of 8 to 100 volume percent of polyolefin, 0 to 40 volume percent of a

substantially inert solid plasticizer, and 0 to 92 volume percent of inert filler material.

6. A semi-permeable membrane according to any of claims 1 to 4, consisting of a homogeneous mixture of 40 to 60 volume percent of polyolefin and 60 to 40 volume percent of an inert filler.

7. A semi-permeable membrane according to claim 6, wherein the plasticizer is polyisobutylene, polybutadiene, polystyrene, atactic polypropylene, ethylene-propylene rubber, or an ethylene-vinyl acetate copolymer.

8. A semi-permeable membrane according to claim 6 or 7, wherein the filler is carbon black, coal dust, graphite, silicon oxide, aluminium oxide, calcium oxide, magnesium oxide, barium oxide, titanium oxide, iron oxide, zinc oxide, tin oxide, calcium carbonate, magnesium carbonate, mica, montmorillonite, kaolin, attapulgite, asbestos, talc, diatomaceous earth, vermiculite, portland cement, calcium silicate, aluminium polysilicate, alumina silica gel, wood flour, wood fibre, glass particles, glass fibres, molybdenum disulphide, zinc sulphide or barium sulphate.

9. A semi-permeable membrane according to any of claims 1 to 8, wherein the essentially flat surface is that of a sheet or a film.

10. A semi-permeable membrane according to any of claims 1 to 9 in the form of a web having a plurality of ribs on at least one of its surfaces, said ribs consisting essentially of the same composition as the web, foamed polypropylene, foamed polyethylene, foamed filled polyethylene or foam filled polyvinyl chloride.

11. A battery separator comprising a semi-permeable membrane claimed in any one of claims 1—10.

12. A battery separator according to claim 11 substantially as hereinbefore described.

13. A process for producing a semi-permeable membrane which comprises blending a composition of from 5 to 65 volume percent of polyolefin having a standard load melt index (as hereinbefore defined) of 0, 5 to 60 volume percent of an inert filler material, and at

- least 30 volume percent of a plasticizer; forming the composition into a web having at least one essentially flat surface; and extracting from the web a portion of the filler or the plasticizer or both, to form a porous battery separator.
- 5 14. A process according to claim 13, wherein the polyolefin is polyethylene, polypropylene, polybutene, an ethylene-propylene copolymer, 10 an ethylene-butene copolymer, a propylene-butene copolymer, or an ethylene-propylene-butene copolymer.
- 15 15. A process according to claim 13 or 14, wherein the polyolefin is a blend of a high molecular weight polyolefin having a standard load melt index of 0 and a low molecular weight polyolefin having a standard load melt index of 0.1 to 5.
- 20 16. A process according to claim 15, wherein each of the blend components is polyethylene.
- 25 17. A process according to any of claims 13 to 16, wherein the filler is water-soluble and is sodium chloride, potassium chloride, calcium chloride, sodium acetate, potassium acetate, calcium acetate, barium acetate, sodium sulphate, potassium sulphate, calcium sulphate, sodium phosphate, potassium phosphate, sodium nitrate, potassium nitrate, sodium carbonate, potassium carbonate or sugar.
- 30 18. A process according to any of claims 13 to 16, wherein the filler is water-insoluble and is carbon black, coal dust, graphite, silicon oxide, aluminium oxide, calcium oxide, magnesium oxide, barium oxide, titanium oxide, iron oxide, zinc oxide, tin oxide, calcium carbonate, magnesium carbonate, mica, montmorillonite, kaolin, attapulgite, asbestos, talc, diatomaceous earth, vermiculite, portland cement, calcium silicate, aluminium polysilicate, alumina silica gel, wood flour, wood fibre, glass particles, glass fibres, molybdenum disulphide, zinc sulphide, or barium sulphate.
- 40 19. A process according to any of claims 13 to 18, wherein the plasticizer is water-soluble and is ethylene glycol, polyethylene glycol, polypropylene glycol, glycerol, triethyl phosphate, polyvinyl alcohol, polyacrylic acid or polyvinyl pyrrolidone.
- 45 20. A process according to any of claims 13 to 18, wherein the plasticizer is water-insoluble and is petroleum oil, wax, asphalt, eicosane, polyisobutylene, polybutadiene, polystyrene, atactic polypropylene, ethylene-propylene rubber, ethylene-vinyl acetate copolymer, oxidized polyethylene, coumarone-indene resin, terpene resin, tall oil, or linseed oil.
- 50 21. A process according to any of claims 13 to 20, wherein the composition comprises 7.5 to 40 volume percent of polyolefin and 10 to 40 volume percent inert filler, the remainder being plasticizer.
- 55 22. A process for producing a semi-permeable membrane according to claim 13 substantially as hereinbefore described.
- 60 65

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